FACTORS INFLUENCING THE SEPARATION OF BINARY MIXTURES BY FRACTIONAL DISTILLATION

BY

WILLIAM MONDENG LANGDON

B.S., University of Illinois, 1935

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1941

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Introduction

The unit operation of fractional distillation is one of great importance in chemical engineering practice. Until very recently, however, the design and operation of rectifying columns have been governed largely by the results of practical experience. The rapid growth of the several industries which employ distillation processes has emphasized the need of a more fundamental and analytical treatment of this problem.

Numerous investigators [1,3,4,7,8,9] have studied the performance of distillation columns. However, the contradictory nature of the results does not permit an insight into the fundamental mechanism of the process. One approach to a solution of this problem has been proposed by Keyes[2], who suggested the factors which might probably influence the performance of the individual plates in a bubble-cap column. According to this proposal, the Murphree plate efficiency[6], which has been generally accepted as a measure of plate performance, should be adopted as the basis of investigation, and experimental study should be directed towards a clarification of the mechanics of rectification and of the relative importance of the various controlling factors.

The present investigation is a continuation of the work initiated by Keyes and Byman[3] and is confined to a study of the continuous rectification of mixtures of isopropyl alcohol and water in a bubble-cap column of four plates. This system was chosen for the present study because the great variation of its physical properties with change in the composition should have a marked effect on column operation.

Experimental

Apparatus: The apparatus used in this work comprised of the following pieces of equipment: still, rectifying column,

total condenser, sight box, reflux and product rotameters, reflux heater, and sample coolers. The column (5 by 9 in. by 4 ft. 11 in. high) contained four, single bubble-cap plates, at spacings of 11 in. Vertical partitions allowed a free vapor space of 5 by 5 in., while 2 in. weirs gave a slot submergence of 1-3/16 in. Each plate was provided with a drain, while liquid samples were taken through screened tubes placed at the center and just under each bubble-cap. Each of the vapor and liquid samples were drawn from the column through a 6 in. length of 3/32 in. copper tubing surrounded by a water-cooled jacket. The entire column was insulated with 2 in. of magnesia lagging and all pipe-lines which carried steam, vapor, or hot liquid were lagged with 1 in. magnesia lagging. Partial condensation in the vapor line to the condenser was prevented by an electrical heating element surrounding it. The condensate leaving the condenser was proportioned by needle-valves into reflux and product streams, whose rates of flow were indicated by calibrated rotameters. The reflux passed through a steam-jacketed preheater, and entered the column at the fourth (top) plate, while the product stream returned directly to the still, together with the liquid reflux from the bottom of the column.

Procedure: Runs were made at reflux ratios (reflux to total vapor) of 1:1, 2:3, and 1:2, covering almost the entire composition range of the binary system, isopropyl alcohol-water. In general, the runs were made at a superficial vapor velocity of 1 ft./sec. In order to determine whether or not entertainment was taking place, runs were also made at velocities varying from 0.5 to 1.2 ft./sec. In the region of the azeotrope, where the difference between vapor and liquid composition was small, most of the runs were made at a reflux ratio of 1:1.

After distillation had begun, the apparatus was operated for a period of one or more hours, during which time only minor adjustments were required to maintain operation under steady conditions. The rectification was continued at steady state for a minimum period of four hours in all cases except when the still liquid was less than 5 mole per cent alcohol. In this case the distillation was continued for ten hours. At

this point temperatures were recorded, and samples were taken. Three sets of samples of 8 ml. each were taken consecutively, except in the case of the preliminary runs where only one or two sets were taken. The compositions of the several samples were obtained from density measurements. The densities were determined to within two parts in fifty thousand using a modified Ostwald type pycnometer.

The plate efficiencies were calculated on the basis of the vapor-liquid equilibrium data determined during the course of this investigation. Both the overall Murphree efficiency in terms of vapor compositions[6], and the overall plate efficiency in terms of liquid compositions[10], were computed directly from the sample compositions and plotted as functions of liquid composition. The corresponding values of local plate efficiency[5] were also calculated and similarly graphed.

Results

A study has been made of the fractional distillation of isopropyl alcohol-water mixtures in a bubble-cap column of four plates, operated without entrainment at superficial vapor velocities, $u = 0.4$ to 1.2 ft./sec., and at reflux ratios (reflux to total vapor) of 1:1, 2:3, and 1:2.

Both the overall Murphree and the local plate efficiency, in terms of vapor composition, have been shown to vary markedly with liquid composition. Changes in reflux ratio and in the rate of distillation (superficial vapor velocity) have very little influence on these efficiencies. At the reflux ratio, $L/V = 1$, the value of the overall Murphree Efficiency is practically constant at 91 per cent over the range of liquid composition, 20 to 55 mole per cent alcohol, decreasing rapidly to 70 at 68 mole per cent alcohol, while the local efficiency shows a more gradual decrease with increasing alcohol concentration, going from 85 at 35 mole per cent to 77 at 55 mole per cent with a sharp break to 63 at 68 mole per cent. For $L/ = 2/3$, the overall efficiency shows a linear decrease from 98 to 91 per cent over the range, 15 to 55 mole per cent alcohol, and was practically coincidental with that for total influx between 55 and 65 mole per cent alsocol, while the curve

for the local efficiency was identical with that for total reflux, being displaced lower by 3 per cent. The curve for the reflux ratio, $L/V = 1/2$, extending over the range, 3 to 40 mole per cent alcohol, shows a more pronounced change, going from an overall efficiency of 220 at the low composition to 95 at the high. The curve for the local efficiency shows the marked effect of the concentration gradients existing on the plate, increasing at approximately the same rate that the overall efficiency decreases to a maximum at 20 mole per cent alcohol.

The corresponding efficiencies in terms of liquid compositions have also been calculated and are compared with the "vapor" efficiencies.

The increase in the overall Murphree efficiency and the decrease in the local efficiency with decreasing reflux ratio may be partially attributed, in the first case, to the difference in the degree of concentration gradients existing on the plates and, in the second case, to variation of effective bubble-cap slot submergence corresponding to decreased liquid hold-up per plate. The influence of the kettle composition on the degree that the operating line approaches the equilibrium curve has been shown to be responsible for large deviations from the mean for reflux ratios of $L/V = 2/3$ and $1/2$.

The significance of physical properties of the liquid in plate-column fractionations is indicated by the pronounced effect of viscosity on the formation of vapor bubbles[11], coupled with the parallel trends of plate efficiency- and viscosity-liquid composition curves.

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VITA

The author was born August 18, 1914, in LaGrange, Illinois. He was educated in the public schools of LaGrange and was graduated from Lyons Township High School of LaGrange in June, 1931. After attending Lyons Township Junior College for two years, he entered the University of Illinois in the fall of 1933 and received the degree of Bachelor of Science in Chemical Engineering in June, 1935. He was connected with the International Harvester Company for two and one-half years, two years being spent in the Metallurgical and Inspection Department of the Wisconsin Steel Works and one-half year in the Analytical Department of the McCormick Works. He was admitted to the Graduate School of the University of Illinois in September, 1937, and received the degree of Master of Science in Chemistry in 1939. He was an assistant in chemistry and chemical engineering during the four academic years of 1937 to 1941.